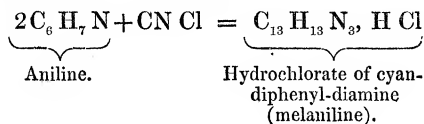


sufficiently well established by their origin, and by the determination of their boiling-points and vapour-densities ; so that the examination of non-volatile bases, retaining one equivalent of unreplaced hydrogen, is not necessary for the elucidation of their atomicity—affording simply additional evidence in favour of facts otherwise satisfactorily proved. But it is obvious how, in the case of compounds of uncertain origin, which may be easily decomposable or difficultly accessible, the formation of this class of salts must facilitate the diagnosis of the diamines, and may, under certain conditions, become the principal criterion for ascertaining the atomicity of an ammonia.

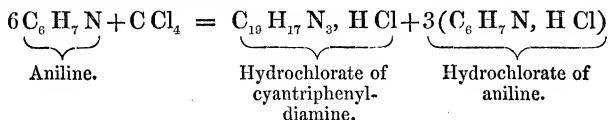
XIII. "Notes of Researches on the Poly-Ammonias."—No.

XV. Monacid Polyamines. By A. W. Hofmann, LL.D.,
F.R.S. Received June 13, 1861.

In former investigations I have pointed out the existence of a group of monacid bases containing three equivalents of nitrogen, the principal representatives of which, cyanodiphenyldiamine and cyantriphenyldiamine, were formed by submitting aniline to the action respectively of chloride of cyanogen *,



and tetrachloride of carbon,



I have lately met again with this group of bases in a new reaction which I beg leave to submit to the Royal Society.

When examining several years ago † the action of ethylate of sodium upon cyanate of ethyl, I observed the formation of triethylamine, but in subsequent experiments ‡ I could not reproduce this compound by

* H=1 ; O=16 ; C=12, &c.

† Proceedings of the Royal Society, vol. viii. p. 489.

‡ Journal of the Chemical Society, vol. xiii. p. 70.

this method, the reaction assuming a totally different form. I have not yet been able to elaborate the circumstances which determine the two different actions, but I have ascertained the nature of the substance which is formed instead of triethylamine.

Cyanate of ethyl, when allowed to flow in a slow stream upon perfectly pure ethylate of sodium, is powerfully acted upon; heat is evolved, which volatilizes a portion of the cyanate of ethyl; by far the larger portion, however, is converted into cyanurate of ethyl, which may be obtained with all its properties, simply by exhausting the dry cake in the retort, after cooling, with cold water.

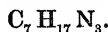
On submitting the mixture of cyanurate of ethyl with ethylate of sodium to distillation at gradually increasing temperatures, ethylene gas is abundantly evolved, while a powerfully alkaline liquid condenses in the receiver, consisting of alcohol, an oily compound easily soluble in alcohol and difficultly soluble in water, ethylamine, and lastly, a powerfully basic oil, which boils at a very high temperature, at which it is partly decomposed.

The basic oil forms a series of saline compounds, amongst which the splendidly crystallized iodide, the beautiful platinum-salt, and the gold-salt deserve to be mentioned. The two latter, on analysis, were found to contain respectively,

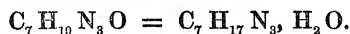
Platinum-salt $C_7H_{17}N_3, HCl, PtCl_2$.

Gold-salt $C_7H_{17}N_3, HCl, AuCl_3$.

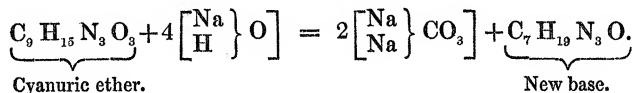
The composition of the base, such as it exists in combination with acids, is thus seen to be represented by the formula



In the free state, however, this substance retains with great pertinacity one molecule of water, being in fact

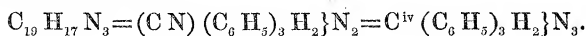


It owes its origin to the gradual action on the cyanurate of ethyl of the hydrated alkali, which is produced by the decomposition of the ethylate of sodium under the influence of heat,



The interpretation of this new compound presents no difficulty.

A glance at the formula shows that it represents in the ethyl-series the body which in the phenyl-series I had previously formed by the action of tetrachloride of carbon on aniline. I have pointed out that the latter may be referred either to two or to three molecules of ammonia, and presents itself respectively as cyantriphenyl-diamine or as carbotriphenyltriamine,



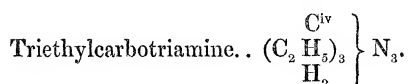
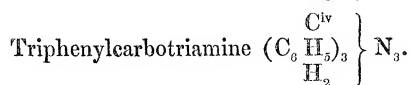
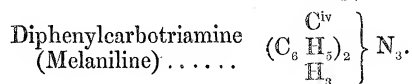
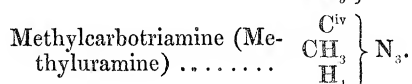
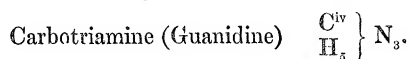
In a similar manner the new ethylated compound may be regarded as cyantriethyl-diamine or carbotriethyltriamine,



The latter formula would illustrate in some measure how the three ammonia-molecules are linked together in these compounds.

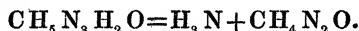
Whatever view may be taken of these bodies, whether they be regarded as diamines or triamines, they claim some interest on account of their well-defined characters and the numerous processes in which they appear to be formed.

Methyluramine, the base discovered by M. Dessaignes among the products of oxidation of creatine, belongs to the same group of bases, and perhaps the most interesting term of the series, guanidine, has been lately obtained by M. Strecker by the action of oxidizing agents upon guanine. Referred to three molecules of ammonia, the several bases which I have mentioned are represented by the following formulæ :—



The perfect analogy of these several compounds is beautifully

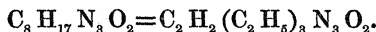
illustrated by the parallelism of their products of decomposition. Thus guanidine, when treated with nitric acid, is transformed into ammonia and urea,



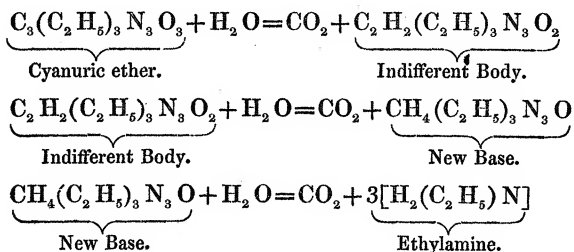
In a similar manner the triethylated compound, when submitted to distillation, splits into ethylamine and diethylurea,



The transformation of cyanuric ether into the new base presents additional interest, inasmuch as it exhibits the passage of this substance into ethylamine under a new aspect. MM. Habich and Limpricht have already pointed out that this transformation is by no means accomplished in one bound, an indifferent intermediate compound being formed, which from its products of decomposition was found to contain

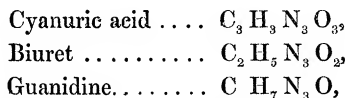


The same oily compound accompanies the new base which is formed by the action of ethylate of sodium upon the cyanurate of ethyl. This substance stands midway between the ethylated base and cyanurate of ethyl, and it is thus seen that the latter passes through two intermediate stages before it is converted into ethylamine, the transformation consisting in the successive assimilation of three molecules of water, which determines the gradual elimination of the carbon of the cyanuric acid in the form of carbonic acid :



In the transformation of cyanuric acid into ammonia, obviously the same succession of changes must be distinguished. In fact the intermediate products are well known, although they have not as yet been obtained directly from cyanuric acid. The first product is the compound discovered by Wiedemann among the products of the

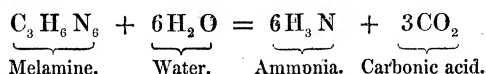
action of heat upon urea (cyanuric acid), and described by him as *biuret*; the second is the *guanidine* of M. Strecker. A glance at their formulæ,



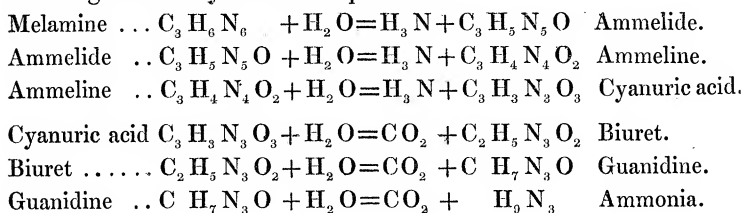
shows that these substances are similarly related to each other as the derivatives of cyanuric ether, and appropriately selected methods will not fail to arrest the reaction at the intermediate stages.

Even now the cyanogen group is particularly rich in examples of serial transformations, accomplished under the influence of successively assimilated water-molecules. Liebig's celebrated researches have shown that melamine before it is converted into cyanuric acid undergoes a series of changes. Fixing water and losing ammonia in the same proportion, melamine is successively converted into ammelide, ammeline, and cyanuric acid. The latter, fixing water and losing carbonic acid instead of ammonia, passes through the intermediate stages, which I have endeavoured to trace, and is ultimately resolved into carbonic acid and ammonia.

The equation



represents the final result of the decomposition of melamine under the influence of the hydrated alkalies, but the water which figures in this equation is fixed, molecule after molecule, and the ultimate products are preceded by not less than five intermediate compounds, the successive formation and decomposition of which is illustrated by the following series of symmetrical equations:—



In carrying out the experiments, which form the subject of this Note, I have been most ably assisted by Dr. C. A. Martius, to whom my best thanks are due for his zealous and skilful co-operation.